

Impregnated activated carbon for environmental protection

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Impregnated activated carbons are carbonaceous adsorbents which have chemicals finely distributed on their internal surface. The impregnation optimizes the existing properties of the activated carbon giving a synergism between the chemicals and the carbon. This facilitates the cost-effective removal of certain impurities from gas streams which would be impossible otherwise. For environmental protection, various qualities of impregnated activated carbon are available and have been used for many years in the fields of gas purification, civil and military gas protection and catalysis.

Keywords: activated carbon; impregnated activated carbon; mercury; hydrogen sulfide; environmental protect

Introduction

Activated carbon is the trade name for a carbonaceous adsorbent which is defined as follows¹: Activated carbons are non-hazardous, processed, carbonaceous products, having a porous structure and a large internal surface area. These materials can adsorb a wide variety of substances, i.e. they are able to attract molecules to their internal surface, and are therefore called adsorbents. The volume of pores of the activated carbons is generally greater than 0.2 ml g⁻¹. The internal surface area is generally greater than 400 m² g⁻¹. The width of the pores ranges from 0.3 to several thousand nm.

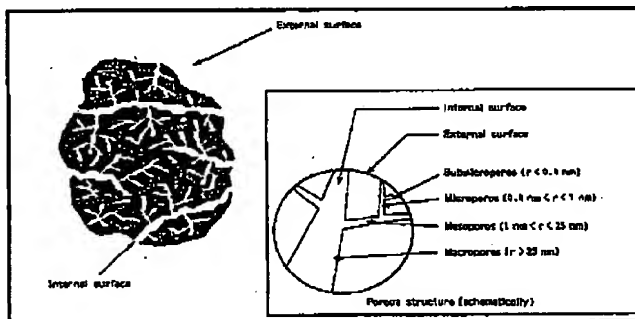


Figure 1: Schematic activated carbon model

All activated carbons are characterized by their ramified pore system within which various mesopores ($r = 1-25$ nm), micropores ($r = 0.4-1.0$ nm) and sub micropores ($r < 0.4$ nm) branch off from what we call macropores ($r > 25$ nm) (Figure 1). Activated carbons have been used for many years quite successfully for adsorptive removal of impurities from exhaust gas and waste water streams. However, for cost-effective removal of certain impurities contained in gases (such as hydrogen sulfide, mercury and ammonia), the adsorption capacities and the feasible removal rates must be substantially boosted by impregnation of the activated carbon by suitable chemicals. When these chemicals are deposited on the internal surface of the activated carbon, the removal mechanism also changes. The impurities are no longer removed by adsorption but by chemisorption.

Three reasons for impregnating activated carbon may be defined, and relevant examples are given below.

1 Optimization of existing properties of activated carbon

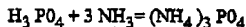
Activated carbons are capable of catalytic oxidation of organic and inorganic compounds. The property of oxidation catalyst can be boosted by, for example, impregnation with potassium iodide acting as promoter. Potassium iodide-impregnated activated carbons are, in fact, already used for catalytic hydrogen sulfide oxidation to elemental sulfur, as described later.

2 Synergism between activated carbon and impregnating agent

Mercury and sulfur are not normally converted to mercury sulfide at ambient temperature. However, if the sulfur is distributed onto the internal surface of activated carbon, this reaction can be run at low temperatures for mercury removal from gases (see description later in this paper).

3 Use of activated carbon as an inert porous carrier material

Activated carbon is used as an inert porous carrier material for distributing chemicals on the large internal surface, thus making them accessible to reactants. For example, activated carbon impregnated with phosphoric acid is used for ammonia removal:



As well as the pore radii distribution of the activated carbon to be impregnated, the chemical composition and the quantity of the impregnation agents used and their distribution in the pore system are very important.

Manufacture

For the manufacture of impregnated activated carbon, an activated carbon of suitable quality for the particular application is impregnated with solutions of salts or other chemicals which, after drying or other after-treatment steps, remain on the internal surface of the activated carbon.

As well as soaking impregnation, spray impregnation can be used. In that case the activated carbon is sprayed in a rotary kiln or in a fluidized bed under defined conditions. The impregnated wet activated carbon needs to be dried in an appropriate installation (e.g. a rotary kiln or fluidized-bed drier). After the drying step, most of the impregnated activated carbons can be used industrially. In some applications the impregnation agents are present in the form of hydroxides, carbonates, chromates or nitrates and must be subjected to thermal after-treatment at higher temperatures (150 to 200°C) to decompose the anions. According to the application, various activated carbons (pellets, granular and powdered qualities) are impregnated with suitable organic or inorganic chemicals.

Homogeneous distribution of the impregnating agents on the internal surface of an activated carbon is important. Furthermore, blocking of the micropores and macropores should be avoided in order to keep the impregnation agent accessible for the reactants. Information on the impregnation agent's distribution and accessibility to the reactants can be obtained in the laboratory by a combination of adsorption and immersion techniques. Bansal *et al.*² and Rebstein and Stoeckli³ examined a sulfur-impregnated activated carbon for mercury removal and demonstrated that the sulfur is predominantly distributed in the micropore system and that no pores are blocked.

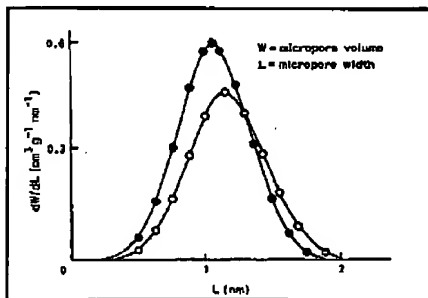


Figure 2: Micropore distribution of basic activated carbon D47/4 (○) and of the same quality impregnated with 15% sulfur (D47/4+S) (□)

Figure 2 shows a comparison of the micropore volume of the initial activated carbon quality D 47/4 and the same activated carbon quality impregnated with 15 % sulfur (D 47/4 + S). The impregnation reduced the micropore system's surface from 742 to 579 m² g⁻¹. Thus, not only does the chemisorption of mercury by sulfur take place, but the adsorptive removal of further gas impurities can also be achieved.

Products and application fields

Impregnated activated carbon is predominantly used in the following application fields (Table 1)^{2,4}

1. Gas purification.
2. Civil and military gas protection.
3. Catalysis.

For these applications the manufacturers offer various qualities of impregnated activated carbon.

Table 1 Typical application fields of impregnated activated carbon

Gas purification	Civil and military gas protection	Catalysis
Application fields:	Application in gas masks, room filters and respiratory apparatus filters:	Application in catalysis:
Hydrogen sulfide	Sulfur dioxide	Vinyl acetate synthesis
Mercaptan	Hydrogen chloride	Vinyl chloride synthesis
Mercury	Hydrogen fluoride	Vinyl fluoride synthesis
Ammonia	Nitrogen oxide	
Amine	Amine	
Acid gases (HCl, SO ₂ , HF, HCN)	Hydrogen sulfide	
Arsine	Mercury	
Phosphine	Radioactive iodine	
Aldehyde	Radioactive methyl iodide	
Radioactive iodine	Phosgene	
Radioactive methyl iodide	Hydrogen cyanide	
Nitrogen oxide	Chlorine	
	Arsine	
	Sarin and other nerve gases	

Table 2 contains a list of frequently used products as well as information on the quality and quantity of the impregnation agents, the basic activated carbon qualities used, and the relevant application fields.

Table 2 Commercial qualities of impregnated activated carbon

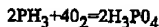
Impregnation			
Chemicals	Quantity (wt%)	Activated carbon ^a	Examples for application

Sulfuric acid	2-25	F 1-4mmØ	Ammonia, amine, mercury
Phosphoric acid	10-30	F 1-4 mm Ø	Ammonia, amine
Potassium carbonate	10-20	F 1-4 mm Ø	Acid gases (HCl, HF, SO ₂ , H ₂ S, NO ₂), carbon disulfide
Iron oxide	10	F 1-4 mm Ø	H ₂ S, mercaptan, COS
Potassium iodide	1-5	F 1-4 mm Ø	H ₂ S, PH ₃ , Hg, AsH ₃ , radioactive gases/radioactive methyl iodide
Triethylene diamine (TEDA)	2-5	F 1-2 mm Ø G 6-16 mesh	Radioactive gases/radioactive methyl iodide
Sulfur	10-20	F 1-4 mm Ø, G	mercury
Potassium permanganate	5	F 3-4 mm Ø	H ₂ S from oxygen-lacking gases
Manganese IV oxide		G 6-16 mesh	Aldehyde
Silver	0.1-3	F 3-4 mm Ø G 8-30 mesh	F: phosphine, arsine G: domestic drinking water filters (oligodynamic effect)
Zinc oxide	10	F 1-4 mm Ø	Hydrogen cyanide
Chromium-copper-silver salts	10-20	F 0.8-3 mm Ø G 12-30 mesh G 6-16 mesh	Civil and military gas protection Phosgene, chlorine, arsine Chloropicrin, sarin and other nerve gases
Mercury II chloride	10-15	F 3-4 mm Ø	Vinyl chloride synthesis Vinyl fluoride synthesis
Zinc acetate	15-25	F 3-4 mm Ø	Vinyl acetate synthesis
Noble metals (palladium, platinum)	1-5	F, G, P	Organic synthesis, hydrogenation

F = pelletized activated carbon G=granulated activated carbon P = powdered activated carbon Ø = pellet diameter

It is obvious that each impregnation agent is frequently used for various purification tasks. The example of the potassium iodide impregnation shows that in these cases a variety of removal mechanisms become effective.

Potassium iodide, as promoter of the oxidation catalyst 'activated carbon', allows catalytic oxidation of hydrogen sulfide to sulfur or of phosphine (PH₃) to phosphoric acid:



Furthermore, potassium iodide-impregnated activated carbon can be used for removal of mercury from gases.

In nuclear power stations, two iodine isotopes (¹³¹I and ¹³³I) are produced during nuclear fission, and this elementary iodine or radioactive methyl iodide may pollute exhaust air streams. For removal of radioactive iodine or methyl iodide, adsorbents are used which contain potassium iodide-impregnated activated carbon. The radioactive iodine is fully removed and deposited onto the activated carbon. With the radioactive methyl iodide to be adsorbed with only low loading rates, an exchange of the radioactive iodine with the inactive iodine of the impregnation agent takes place (isotope exchange). Owing to the low half life period of the iodine isotopes (¹³¹I = 8.04 days, ¹³³I = 21 h), the loaded activated carbon rapidly becomes inactive.

For each of these three application fields for potassium iodide-impregnated activated carbons, it should be noted that a different basic activated carbon, optimized for the intended task, is impregnated with potassium iodide.

Two examples from the field of environmental protection, namely mercury and hydrogen sulfide removal from gases, may explain the development and use of impregnated activated carbon and provide advice on the design of adsorbents.

Mercury removal

In contrast to all other metals, mercury is in the liquid state at room temperature and has a relatively high vapour pressure of 171 Pa (15 mg m⁻³) at 20°C. Apart from problems caused by the toxic properties of mercury and its other environmental hazards, traces of mercury can poison many industrial catalytic processes. For mercury removal from gases, wet processes (oxidizing gas scrubbing) as well as dry processes (adsorption processes) are in operation.

Development of optimized adsorbents

For developing impregnated activated carbon qualities for mercury removal, the basic activated carbon quality D 47/4 has been impregnated with a variety of chemicals⁵. The removal performance of the adsorbents has been tested under dynamic conditions (Table 3).

Table 3 Test conditions for mercury removal

Parameters	
Hg-content in the raw gas (mg m ⁻³)	2.2 ± 0.5
Temperature (K)	298
Bed depth (m)	0.2
Velocity of flow (m s ⁻¹)	0.3
Residence time (s)	0.66
Method of analysis	AAS

The non-treated activated carbon D 47/4 is basically suited for adsorptive removal of mercury from waste air streams. The mercury removal rate may be read from Figure 3 as a function of the testing period. Because of the long useful life of the adsorbents, the test period was plotted on a logarithmic scale. The test was stopped at a mercury-breakthrough rate of 50% after 130 h. It was found earlier that iodine impregnation of activated carbon results in substantial improvement of the mercury adsorption capacity. These iodine-impregnated activated carbon qualities were first used as filter materials in breathing apparatus allowing a safe stay in mercury vapour contaminated rooms. As shown in Figure 3, the purification performance and the useful life of the D 47/4 activated carbon is substantially boosted by impregnation with 2 wt% potassium iodide. Possibly, the mercury reacts under the catalytic influence of the activated carbon to form mercury iodide. The adsorption mechanisms of the iodine-treated activated carbon surface has not yet been explained.

If activated carbon is impregnated with sulfuric acid, the mercury elimination rate and, above all, the adsorption capacity are substantially boosted (Figure 3).

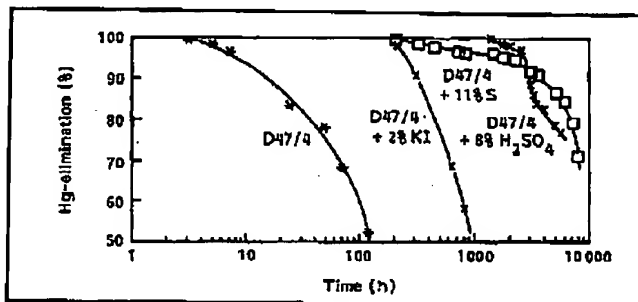
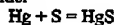


Figure 3 Mercury elimination rates of non-impregnated and impregnated activated carbon

The suitability of sulfur-impregnated activated carbon was described in 1972 by Sinha and Walker⁶. Sulfur impregnation yields a product which, from a corrosion technical viewpoint, is safe. As shown by the example of the D 47/4 activated carbon impregnated with 11% sulfur, mercury elimination rates > 90% were still recorded even after 3000 hours of test. Thus sulfur impregnated activated carbon qualities are suitable and commercially available-adsorbents for mercury removal.

The mercury vapour diffused into the activated carbon's pore system reacts, under the catalytic effect of the activated carbon, with the sulfur distributed on the internal surface to form mercury sulfide:



The kinetics are limited by the following mass transport steps:

1. Diffusion of mercury to the external surface of the activated carbon.
2. Diffusion of mercury into the pores.
3. Adsorption of mercury at the active sites of the activated carbon.
4. Chemisorption of mercury by sulfur.

These kinetic conditions mean increased mercury elimination rates as a function of decreased particle size. In the commercial use of adsorbents with small particle size, a higher elimination rate is obtained with identical bed height, but a higher pressure drop has to be overcome. Mercury chemisorption can only take place as long as the accessible surface of the sulfur distributed on the internal activated carbon surface is covered with a monomolecular layer. In the case of an 11 wt% adsorbed sulfur, a stoichiometric mercury adsorption of 79 wt% is attained theoretically. If the sulfur dispersity is assumed to be 0.3-0.5, mercury loads of 20-35 wt% can be expected in practice.

Table 4 contains a comparison of the advantages and disadvantages of different impregnated activated carbon qualities in terms of purification efficiency, adsorption capacity and corrosion problems. It is obvious that impregnated activated carbon is an advantageous means of mercury removal.

Table 4 Impregnated activated carbon qualities for mercury removal

Test results			
Impregnation agent	Purification efficiency	Adsorption capacity	Corrosion problems
None	Poor	Poor	None
Potassium iodide	Good	Good	None
Sulfuric acid	Good	Very good	Possible

Sulfur	Very good	Very good	None
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Application examples

As mercury or mercury-contaminated raw materials are used in numerous industrial processes, mercury is often released via waste water and waste air. Mercury emissions mainly originate from the following processes:

1. Plants for fossil fuel and waste combustion.
2. Alkali chloride-electrolyses according to the mercury cell process.
3. Battery and catalyst factories.
4. Production of mercury-containing chemicals and fungicides.
5. Production of electric switches, measuring instruments and fluorescent lamps.
6. Mercury removal from natural gas.
7. Waste gases from plants for recycling fluorescent lamps and batteries.
8. Plants for thermal decontamination of soils.

A design example for mercury removal (Table 5) shows the advantages of impregnated activated carbon; mercury removal plants are often of simple design, consisting only of a fan and the adsorber. For purification of a $10\,000\text{ m}^3\text{ h}^{-1}$ gas stream with a mercury concentration of $\sim 2.5\text{ mg m}^{-3}$ only one adsorber with a diameter of 3 m and a bed height of 0.6 m is required. Over a service life of 8000 h, a removal rate $>98\%$ can be obtained.

Table 5 Design example for mercury removal

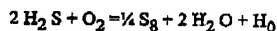
Parameters	
Gas stream ($\text{m}^3\text{ h}^{-1}$)	1
Mercury content (mg m^{-3})	2.5
Service life (h)	8000
Purification efficiency (%)	>98
Adsorber design	
Adsorber flow area (m^2)	7
Bed depth (m)	0.6
Adsorbent requirement (mt/ year)	25
Activated carbon	D 47/4 + S

Hydrogen sulfide removal

All natural or synthesis gases originating or made from sulfur-containing raw materials contain hydrogen sulfide (H_2S) in various concentrations. Owing to the high toxicity of H_2S (5000 ppm of H_2S are lethal within seconds), its environmental impact (0.02 ppm smell threshold), its effect as a catalyst poison and for reasons of corrosion protection, all H_2S has to be removed prior to the use or transport of the gases.

Catalytic hydrogen sulfide oxidation

A dry blend of H_2S and oxygen does not react at ambient temperature, but only at temperatures above 200°C . However, in the presence of activated carbon, H_2S reacts with oxygen at low temperatures to produce sulfur and water:



($H_0 = -444 \text{ kJ}$)

The sulfur produced is adsorbed on the internal surface of the activated carbon and the water is desorbed from the catalyst surface^{7,9}. It is possible to obtain a load consisting of up to 100% by weight of sulfur.

In Figure 4 a scheme is displayed which explains a possible mechanism proposed by Hedden *et al.*⁸ for H_2S oxidation on activated carbon. A water film is formed on the surface of the activated carbon. In this water film the reactants H_2S and oxygen are dissolved. The oxygen molecules are adsorbed on the activated carbon surface and broken into reactive radicals. This oxygen activation by the activated carbon is the actual catalytic step.

The H_2S molecules are partly dissociated into protons and hydrosulfide ions. The latter react with the oxygen radicals to form hydroxyl ions and sulfur which is adsorbed on the activated carbon. The protons neutralize the hydroxyl ions thus producing water.

For boosting the activity of the oxidation catalyst activated carbon-a large variety of promoters were tested. For H_2S removal, activated carbon qualities impregnated with ~ 10 wt% Fe_2O_3 are used. The use of an iron salt as promoter is judged differently from others since, on one hand, the reaction velocity of H_2S oxidation is increased, but on the other hand, oxidation of the H_2S via sulfur up to the production of sulfuric acid is promoted. Potassium iodide impregnation of activated carbon gained industrial importance because the promoter not only increases the reaction velocity but also inhibits the formation of sulfuric acid by unwanted side-reactions. Figure 5 shows the integral sulfur pick-up of a non-impregnated activated carbon and of an activated carbon impregnated with ~ 2 wt% potassium iodide at reaction temperatures of 70 and 125°C and as a function of the test period. Potassium iodide as promoter clearly effects a more rapid sulfur removal onto the activated carbon catalyst.

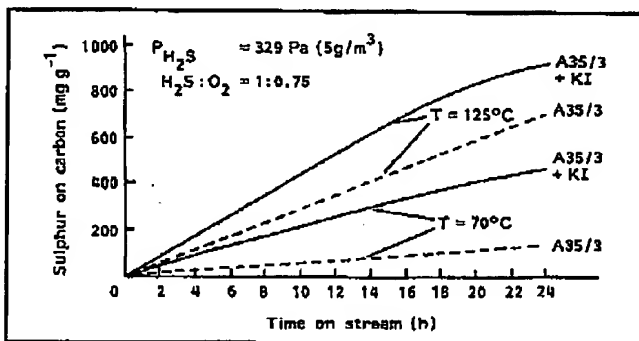
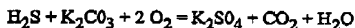


Figure 5 Influence of temperature and promoter on activity

Besides the above-described catalytic H_2S oxidation, other reactions on impregnated activated carbon can be used for H_2S removal. At higher temperatures ($T > 50^\circ\text{C}$) and in the presence of water vapour, H_2S can also be removed onto activated carbon impregnated with potassium carbonate (Desorex process4):



The spent activated carbon may be regenerated by scrubbing with water. After a potassium carbonate 'freshing-up' impregnation, the activated carbon can be used again. For removal of low H_2S concentrations from oxygen-free gases (such as carbon dioxide), frequent use is made of activated carbon impregnated with potassium permanganate. Potassium permanganate is converted during impregnation to manganese dioxide which effects H_2S oxidation.

Application examples

For many years, impregnated activated carbon qualities have been used in the temperature range between 20 and 100°C for H₂S removal from industrial gases. Typical application fields of Activated carbon removal are:

1. Waste gases in viscose industries (Sulfosorbon and Thiocarb processes).
2. Residual gases from Claus processes. Synthetic gas purification.
3. Natural gas purification.
4. Landfill gases and sewer gases.

Table 6 Design example for H₂S removal

Parameters	
Gas stream (m ³ h ⁻¹)	500
H ₂ S content (mg m ⁻³)	200
Temperature (°C)	70
Service life (h)	4000
Adsorber design	
Adsorber flow area (m ²)	1.4
Bed depth (m)	2.5
Activated carbon	C38/4+KI
Activated carbon content (t)	1.4

The design example of H₂S removal from landfill gas (Table 6) shows the use of impregnated activated carbon. The H₂S concentration of 200 mg m⁻³ of a 500 m³ h⁻¹ gas stream must be reduced to a value of less than 0.1 mg m⁻³. For reliable desulfurization over a useful bed-life of about 4000 h, only one adsorber with 1.4 m of diameter and 2.5 m of bed height is required.

Please do not hesitate to contact us via [Carbon Link](#) with any of your queries related to this subject matter or any other activated carbon issue.

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